

US009636664B1

(12) United States Patent

Habas et al.

(10) Patent No.: US 9,636,664 B1 (45) Date of Patent: May 2, 2017

(54) METAL PHOSPHIDE CATALYSTS AND METHODS FOR MAKING THE SAME AND USES THEREOF

(71) Applicant: Alliance for Sustainable Energy, LLC, Golden, CO (US)

(72) Inventors: Susan Ellen Habas, Arvada, CO (US);
Jun Wang, Highlands Ranch, CO (US);
Daniel A. Ruddy, Arvada, CO (US);
Frederick Raymond Gabriel
Baddour, Denver, CO (US); Joshua

(73) Assignee: Alliance for Sustainable Energy, LLC, Golden, CO (US)

Schaidle, Arvada, CO (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35

U.S.C. 154(b) by 0 days.

(21) Appl. No.: 15/174,691

(22) Filed: Jun. 6, 2016

Related U.S. Application Data

(60) Provisional application No. 62/170,906, filed on Jun. 4, 2015.

(51) Int. Cl.

B01J 27/19 (2006.01)

C01B 25/08 (2006.01)

B01J 27/185 (2006.01)

B01J 35/00 (2006.01)

B01J 37/08 (2006.01)

C10G 3/00 (2006.01)

(52) U.S. Cl.

(58) Field of Classification Search

None

See application file for complete search history.

(56) References Cited

U.S. PATENT DOCUMENTS

4,185,081 A 1/1980 Fauth et al. 5,688,909 A 11/1997 Drent et al. 7,446,075 B1 11/2008 Kolev 8,465,716 B2 6/2013 Le Floch et al. 8,753,592 B2 6/2014 Strupeit et al. 2014/0150332 A1 6/2014 Lee et al.

FOREIGN PATENT DOCUMENTS

WO WO 01/23501 A1 4/2001 WO WO 2010/071459 A1 6/2010

OTHER PUBLICATIONS

Balli et al., "Magnetocaloric Effect in Ternary Metal Phosphides (Fe_{1-x}Ni_x)₂P", Journal of Magnetism and Magnetic Materials, 2007, vol. 316, pp. 358-360.

Callejas et al., "Electrocatalytic and Photocatalytic Hydrogen Production from Acidic and Neutral-pH Aqueous Solutions Using Iron Phosphide Nanoparticles", ACS Nano, 2014, vol. 8, No. 11, pp. 11101-11107

Carenco et al., "Controlled Design of Size-Tunable Monodisperse Nickel Nanoparticles", Chemistry of Materials, 2010, vol. 22, pp. 1340-1349.

Carenco et al., "Magnetic Core—Shell Nanoparticles from Nanoscaled-Induced Phase Segregation", Chemistry of Materials, 2011, vol. 23, pp. 2270-2277.

Carenco et al., "Nanoscaled Metal Borides and Phosphides: Recent Developments and Perspectives", Chemical Reviews, 2013, vol. 113, pp. 7981-8065.

Gaudette et al., "Mössbauer Spectroscopy Investigation and Hydrodesulfurization Properties of Iron-Nickel Phosphide Catalysts", Journal of Catalysis, 2010, vol. 272, pp. 18-27.

Ha et al., "The Structural Evolution and Diffusion During the Chemical Transformation 2015 from Cobalt to Cobalt Phosphide Nanoparticles", Journal of Materials Chemistry, 2011, vol. 21, pp. 11498-11510.

Habas et al., "A Facile Molecular Precursor Route to Metal Phosphide Nanoparticles and Their Evaluation as Hydrodeoxygenation Catalysts", Chemistry Materials, 2015, vol. 27, pp. 7580-7592.

Henkes et al., "Converting Metals into Phosphides: A General Strategy for the Synthesis of Metal Phosphide Nanocrystals", Journal of the American Chemical Society, 2007, vol. 129, No. 7, pp. 1896-1897.

Henkes et al., "Trioctylphosphine: A General Phosphorus Source for the Low-Temperature Conversion of Metals into Metal Phosphides", Chemistry of Materials, 2007, vol. 19, No. 17, pp. 4234-4242.

Henkes et al., "Template-Assisted Synthesis of Shape-Controlled Rh₂P Nanocrystals", Inorganic Chemistry, 2008, vol. 47, pp. 671-

Hitihami-Mudiyanselage et al., "Synthesis and Characterization of Discrete Fe_xNi_{2-x}P Nanocrystals (0<x<2): Compositional Effects on Magnetic Properties", Chemistry of Materials, 2015, vol. 27, pp. 6592-6600

Jiang et al., "One-pot Synthesis of Carbon-coated Ni₅P₄ Nanoparticles and CoP Nanorods for High-rate and High-stability Lithium-ion Batteries", Journal of Materials Chemistry A, 2015, vol. 3, pp. 23345-23351.

Jürgens et al., "Colloidally Prepared Nanoparticles for the Synthesis of Structurally Well-Defined and Highly Active Heterogeneous Catalysts", Angewandte Chemie International Edition, 2008, vol. 47, pp. 8946-8949.

(Continued)

Primary Examiner — Yun Qian

(74) Attorney, Agent, or Firm — Michael A. McIntyre

(57) ABSTRACT

The present disclosure relates to a method that includes heating a mixture that includes a metal phenylphosphine-containing precursor that includes at least one of Mo(PPh₃)₂ (CO)₄, Pd(PPh₃)₄, Ru(PPh₃)₃Cl₂, Ru(PPh₃)₂(CO)₂Cl₂, Co(PPh₃)(CO)₂(NO), and/or Rh(PPh₃)₂(CO)Cl, a surfactant, and a solvent. The heating is to a target temperature to form a heated mixture containing a metal phosphide nanoparticle that includes at least one of MoP, Ru₂P, Co₂P, Rh₂P, and/or Pd₃P, and the metal phosphide nanoparticle is not hollow.

6 Claims, 21 Drawing Sheets